



# A One-Pot Tandem Olefin Isomerization/Metathesis-Coupling (ISOMET) Reaction

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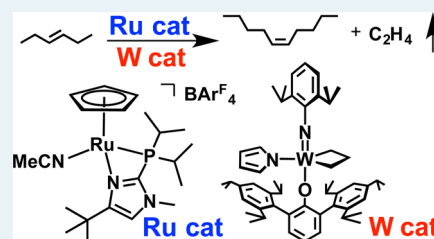
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## S Supporting Information

**ABSTRACT:** A tandem catalytic reaction has been developed as part of a process to discover tungsten-based olefin metathesis catalysts that have a strong preference for terminal olefins over *cis* or *trans* internal isomers in olefin metathesis. This tandem isomerization/terminal olefin metathesis reaction (ISOMET) converts  $C_n$  *trans* internal olefins into  $C_{2n-2}$  *cis* olefins and ethylene. This reaction is made possible with Ru-based “alkene zipper” catalysts, which selectively isomerize *trans* olefins to an equilibrium mixture of *trans* and terminal olefins, plus tungsten-based metathesis catalysts that react relatively selectively with terminal olefins to give Z homocoupled products. The most effective catalysts are  $W(NAr)(C_3H_6)(pyr)-(OHIPT)$  (Ar = 2,6-diisopropylphenyl; pyr = pyrrolide; OHIPT = O-2,6-(2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and various  $[CpRu(P-N)(MeCN)]X$  ( $X^- = [B(3,5-(CF_3)_2C_6H_3)_4]^-$ ,  $PF_6^-$ ,  $B(C_6F_5)_4^-$ ) isomerization catalysts.

**KEYWORDS:** tandem catalysis, olefin, metathesis, isomerization, ruthenium, tungsten



## INTRODUCTION

Alkane Metathesis (AM)<sup>1</sup> reactions and variations such as the alkyl group cross-metathesis reaction<sup>2</sup> that employ an Ir dehydrogenation catalyst and a Mo-based or W-based olefin metathesis catalyst create new hydrocarbons directly from alkanes via an alkane dehydrogenation/olefin metathesis/olefin hydrogenation sequence.<sup>3</sup> An example is conversion of octane into a mixture that contains linear alkanes from ethane to alkanes as large as a C<sub>25</sub>. AM is a relatively recent example of what have been called concurrent or orthogonal tandem catalytic reactions.<sup>4</sup> While the total turnovers have been improved through the development of more thermally robust tungsten-based metathesis catalysts,<sup>5</sup> a significant limitation is still a lack of selectivity for forming a relatively small selection of higher molecular weight alkanes. The most selective catalyst is still Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>6</sup> although it is not the most stable under the reaction conditions and the highest turnovers are not realized with this catalyst.

In an ideal AM reaction, an alkane of chain length  $C_n$  is converted to a  $C_{2n-2}$  alkane, with ethane as the only byproduct (Scheme 1, top); secondary metathesis could generate additional products, e.g.,  $C_{3n-3}$ ,  $C_{4n-4}$ ... but these products would be minor components at low conversions. Current AM reactions feature many more products than the  $C_{2n-2}$ ,  $C_{3n-3}$ ,  $C_{4n-4}$ ... series (Scheme 1, bottom), in part due to the formation of intermediate internal olefins through dehydrogenation of alkanes at internal positions, or by rapid isomerization of olefins (probably largely by Ir) to the thermodynamic mixture of olefins, a distribution that contains only ~1% terminal olefin.

Internal olefins undergo cross-metathesis to afford a range of olefin chain lengths, which upon hydrogenation lead to the observed mixture of alkanes in current AM reactions of this type. AM selectivity could be improved by preventing the cross-metathesis of internal olefins. Therefore, a possible solution would be to employ a metathesis catalyst that would react only with the small quantity of terminal  $C_n$  olefins present to yield ethylene and a  $C_{2n-2}$  internal olefin that would then be rehydrogenated to yield ethane and a  $C_{2n-2}$  alkane. If ethane were removed at some controlled rate, and if methods were developed to prevent formation of very long alkanes, then a relatively small collection of long alkanes could be formed through homocoupling and cross-coupling of intermediate terminal olefins.

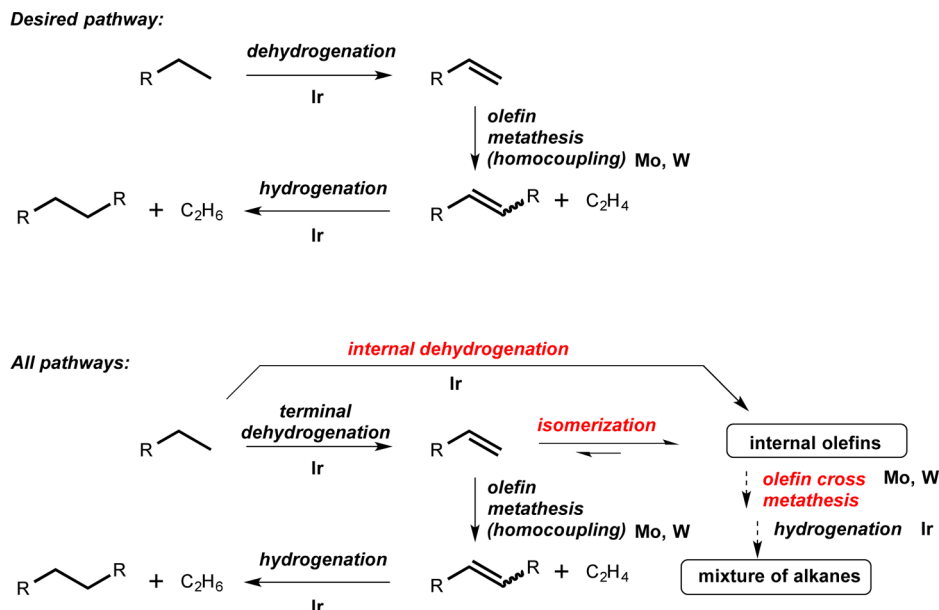
In order to test the principle of this approach, we turned to an exploration of a tandem process that would produce a small amount of terminal olefins through rapid isomerization reactions in the presence of a metathesis catalyst that is selective for metathesis of terminal olefins in an equilibrium mixture of all possible olefins formed through double bond isomerization. Among the other known tandem reactions of this general type (Scheme 2) is tandem isomerization/hydroformylation, an industrially relevant process with extensive precedent.<sup>7</sup> Several other isomerization/terminal functionalization strategies have been reported in the

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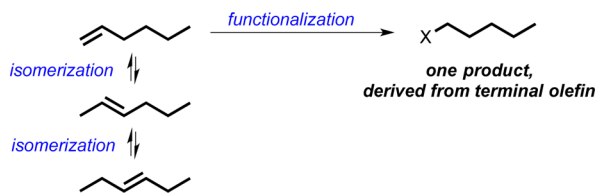
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Scheme 1. Desired (Top) and Complete (Bottom) Pathways Operating in the Alkane Metathesis (AM) Reaction



Scheme 2. Tandem Isomerization/Functionalization Reactions



literature,<sup>8</sup> and a few are organometallic in nature, such as a Rh-catalyzed tandem isomerization/hydroformylation/reductive amination demonstrated by Beller and co-workers<sup>9</sup> and a tandem isomerization/hydroboration reaction reported by Chirik and Obligation.<sup>10</sup>

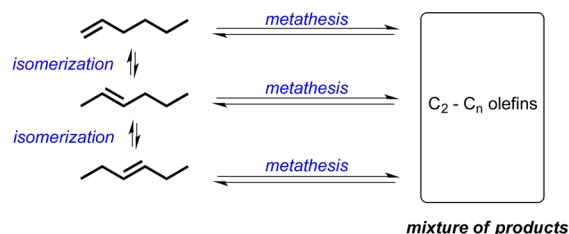
Sustained efforts in metathesis research have resulted in the development of highly selective Mo and W catalysts for the synthesis of *Z*-olefins.<sup>11</sup> Although *Z*-selective metathesis and asymmetric metathesis (catalyst stereoselectivity)<sup>12</sup> are now relatively well-known, our understanding of the differences in reactivity between terminal, *cis* internal, and *trans* internal olefins (catalyst chemoselectivity) remains relatively underdeveloped. Catalysts that can provide high levels of *Z* products over extended reaction periods must be relatively inactive for the *Z*-to-*E* postmetathesis isomerization of internal olefins; therefore *Z*-selective catalysts may exhibit some level of terminal olefin selectivity.<sup>13</sup> Selectivity for terminal olefins is valuable in the homometathesis of conjugated dienes to form trienes, where Mo and W monoalkoxide pyrrolide (MAP) complexes demonstrate high chemoselectivity for terminal olefins.<sup>14</sup> In related work, certain Ru metathesis catalysts can discriminate between internal and terminal olefins in unconjugated dienes.<sup>15</sup> In general, terminal olefins could be generated through isomerization of internal olefins and then immediately and selectively homometathesized *in situ*.

Isomerization and olefin metathesis have previously been employed together in tandem reactions, but so far, all examples differ from the isomerization/terminal functionalization goal described above; i.e., all olefins, internal and terminal, are metathesized *in situ*. In the Shell Higher Olefins Process

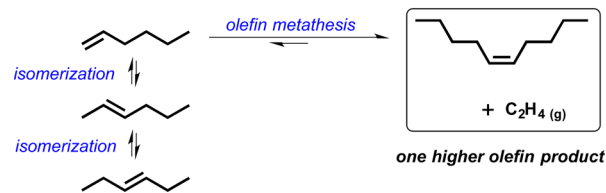
(SHOP), olefins that are derived through ethylene oligomerization are manipulated through subsequent olefin metathesis.<sup>16</sup> Gooßen and co-workers used a Ru metathesis catalyst and a Pd olefin isomerization catalyst to afford a distribution of olefins from a single olefin, a process they called “isomerizing self-metathesis” (Scheme 3A).<sup>17</sup> The work reported here builds on

Scheme 3. Previous Isomerizing Self-Metatheses versus Selective Isomerization/Metathesis (ISOMET)

## A. Previous isomerizing self-metatheses



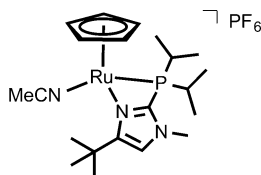
## B. Selective isomerization/metathesis (ISOMET)



previous incarnations of isomerization/cross-metathesis, where many different olefin chain lengths are produced from a single species.<sup>18</sup> To our knowledge, there are no previous reports of a tandem isomerization/metathesis (ISOMET) process where terminal olefins are selectively metathesized to afford a single internal olefin (Scheme 3B).

As illustrated in Scheme 3B, an ISOMET reaction can be envisioned in which a *cis* internal olefin is formed from a mixture of *trans* olefins. This seems possible as a consequence of the development of Mo or W olefin metathesis catalysts that

are *Z*-selective and “alkene zipper” Ru complexes<sup>19</sup> that are effective for selective (*trans* to *trans*) positional isomerization of *trans* olefins over *cis* positional or geometrical isomers (Figure 1).<sup>18c</sup> *Trans*-selective Ru olefin isomerization catalysts should



**Figure 1.** An “alkene zipper” Ru isomerization catalyst.

not react with *cis* olefins that are formed through *Z*-selective homocoupling of terminal olefins. Finally, the isomerization and metathesis catalysts obviously must be mutually compatible and carry out their selective functions in the presence of one another. The amount of terminal olefin in an equilibrium mixture can be estimated using a calculated product distribution derived from standard enthalpies of formation.<sup>20</sup> For a mixture of 1-hexene, *trans*-2-hexene, and *trans*-3-hexene, approximately 1% of the total distribution is 1-hexene at 298 K (Table 1). Clearly a metathesis catalyst is required that has a dramatic preference (preferably >1000) for metathesis homocoupling of the terminal olefin in the presence of internal olefins.

This report discusses the ISOMET strategy for exploring metathesis chemoselectivity and demonstrates the catalytic utility of this tandem process for the generation of higher *Z*-olefins from mixtures of *trans* internal olefins.

## RESULTS AND DISCUSSION

**Development of the ISOMET Method.** The primary objective is to measure *cis* selectivity and terminal selectivity in an ISOMET reaction. *Trans*-3-hexene was chosen as the internal olefin because it is relatively inexpensive compared to other pure *trans* olefins; ethylene and *cis*-5-decene would be formed from *trans*-3-hexene in the ISOMET reaction.

In an early stage of our investigation of metathesis chemoselectivity, W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (OHIPT = O-2,6-(2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> were each treated with various ratios of 1-octene and *trans*-2-octene (Table 2). W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) has previously been shown to react selectively with terminal olefins over internal olefins in the room temperature homocoupling of dienes<sup>14</sup> and also exhibits chain length selectivity in the alkyl group cross-metathesis reaction.<sup>2</sup> W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) was almost completely unreactive toward internal olefins at a 50:1 ratio of internal olefin to terminal olefin. Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> was far less selective. Therefore, W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)-

**Table 2.** Competition Experiment between 1-Octene and *trans*-2-Octene Using Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> and W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT)<sup>a</sup>

catalyst	ratio of <i>trans</i> -2-octene/1-octene	1-octene consumed	<i>trans</i> -2-octene consumed
Mo(NAr)(CHCMe <sub>2</sub> Ph)[OC(CF <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub>	10:1	50%	48%
Mo(NAr)(CHCMe <sub>2</sub> Ph)[OC(CF <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub>	50:1	>99%	58%
W(NAr)(C <sub>3</sub> H <sub>6</sub> )(pyr)(OHIPT)	10:1	60%	
W(NAr)(C <sub>3</sub> H <sub>6</sub> )(pyr)(OHIPT)	50:1	50%	2%

<sup>a</sup>1-Octene and *trans*-2-octene, C<sub>6</sub>D<sub>6</sub>, W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (2.5 mg, 2.6 μmol) or Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (2.5 mg, 3.3 μmol), RT, closed vial.

(OHIPT) was chosen as the first generation catalyst for the ISOMET reaction.

Trials were performed first in open vials at room temperature, or in closed systems (e.g., J. Young NMR tubes); these reactions gave little product. In order to remove ethylene continuously, argon gas was passed slowly through the headspace of a refluxing solution that contained the two required catalysts. Dichloromethane was added to limit the temperature for the ISOMET reaction to 40 °C and to dissolve [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup>.

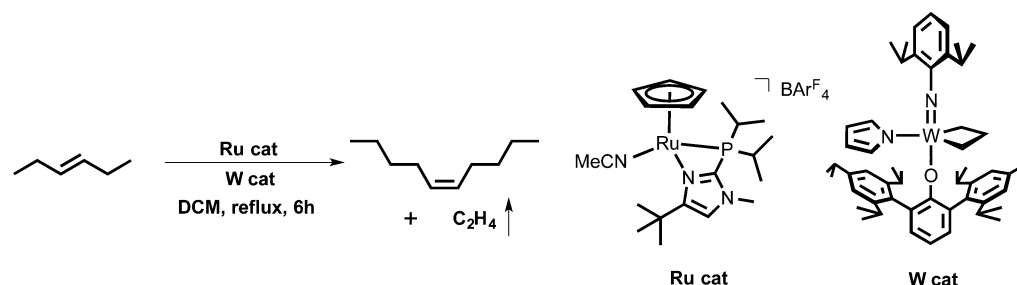
We first investigated various loadings of W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) and [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup> (Scheme 4; Table 3). The *cis* selectivity was estimated by dividing the *cis*-5-decene fraction by the total decene (C10) fractions; all olefins were quantified through GC experiments. The C7–C10 olefins were the major products, so chain length selectivity was calculated from the ratio of C10 products versus the sum of the C7–C10 products. Reducing the [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup> loading from 0.10 mol % to 0.05 mol % did not reduce the amount of C10 product; loadings lower than 0.05 mol % were not attempted. An increase in tungsten catalyst loading increased the C10 product and slightly decreased the chain length selectivity.

The major C9 product produced in ISOMET is most likely *cis*-4-nonene, which can be formed through the cross-metathesis of 1-hexene and *trans*-2-hexene. While the homocoupling of 1-hexene is highly *Z*-selective, 1-hexene/*trans*-2-hexene cross-metathesis is much less *Z*-selective. This result can be rationalized by considering the possible approaches of *trans*-2-hexene to an *n*-pentylidene complex (Scheme 5). Both approaches would lead to a tungstacyclobutane whose substituents point toward the bulky apical OHIPT ligand, so there is less of an energy difference between the two approaches than would be expected in a homometathesis of terminal olefins, where *Z*-selectivity is high. Increasing the bulk

**Table 1.** Calculated Product Distribution of Hexene Isomers at 298 K<sup>a</sup>

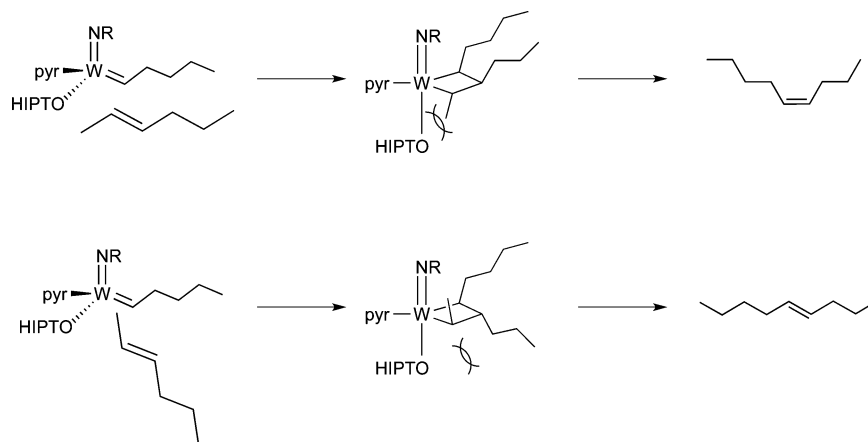
isomer	ΔH <sub>f</sub> <sup>°</sup>	ΔΔH <sub>f</sub> <sup>°</sup>	B <sub>f</sub>	D	B <sub>f</sub> × D	calcd (%)	found (%) <sup>b</sup>
1-hexene	−17.29	2.6	0.0123	2	0.0248	0.93	0.96
<i>t</i> -2-hexene	−19.89	0	1	2	2	74.9	74.1
<i>t</i> -3-hexene	−19.63	0.26	0.645	1	0.645	24.1	25.0

<sup>a</sup>Adapted from the approach of Morrill et al.<sup>20</sup> for the equilibrium distribution of heptenes. Definitions: ΔH<sub>f</sub> = standard enthalpies of formation of isomeric hexenes in kcal/mol;<sup>25</sup> B<sub>f</sub> = Boltzmann factor = exp(−ΔΔH<sub>f</sub>/RT); D = degeneracy. <sup>b</sup>Product distribution employing [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup>.

Scheme 4. ISOMET Reaction of *trans*-3-HexeneTable 3. Effect of Catalyst Loading on the ISOMET Reaction of *trans*-3-Hexene<sup>a</sup>

W loading	Ru loading	<i>cis</i> -5-decene (mmol)	C10 (mmol)	% <i>cis</i> <sup>b</sup>	% chain length selectivity <sup>c</sup>	W TON <sup>d</sup>	Ru TON <sup>d</sup>
0.16 mol %	0.1 mol %	0.247 ± 0.056 <sup>e</sup>	0.263 ± 0.062	94 ± 1%	64%	48 ± 11	95 ± 21
0.16 mol %	0.05 mol %	0.342	0.368	93%	64%	67	263
0.32 mol %	0.05 mol %	0.459	0.496	93%	59%	45	353

<sup>a</sup>[CpRu(P-N)(MeCN)]BARF<sub>4</sub>, W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT), 350 mg *trans*-3-hexene, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 6h. <sup>b</sup>Measured as the ratio of *cis*-5-decene versus the total C10 product formed. <sup>c</sup>Measured as the ratio of C10 product versus the total C7, C8, C9, and C10 product formed. <sup>d</sup>Calculated with respect to *cis*-5-decene. <sup>e</sup>Average of three runs.

Scheme 5. Reaction of an *n*-Pentylidene with *trans*-2-Hexene

of the phenoxide ligand even further might be a way to increase the selectivity for terminal olefins, but the consequence would likely be a decrease in the overall rate of reaction.

If the ISOMET reaction is performed at room temperature rather than at 40 °C, the conversion is much lower (0.018 mmol *cis*-5-decene at 22 °C vs 0.250 mmol at 40 °C). While a loss of ethylene undoubtedly is crucial for efficient olefin metathesis, the ratio of hexene products observed in the room temperature reaction is far from equilibrium, a finding consistent with ethylene inhibition. Attempts to perform ISOMET under a dynamic vacuum at room temperature were unsuccessful; substrate was lost readily. An attempt to carry out the reaction at 0 °C yielded no product.

While *cis* selectivity and chain length selectivity are similar from run to run, the conversion varies considerably from one trial to another. Several explanations are possible. Isomerization and metathesis can proceed prior to heating the reaction, and the amount of time that elapses from preparation of the reaction to heating may range from 5 to 10 min per reaction as the reactor is moved from the glovebox to a heat source. Because some dichloromethane will evaporate during the reaction, the rate of change in solution concentration and the rate of ethylene loss may differ from run to run.

Various W complexes were investigated in the ISOMET reaction (Table 4). The TON per W and TON per Ru are calculated with respect to the *cis*-5-decene formed in an ideal ISOMET reaction, rather than with respect to the sum of all products. There is a strong correlation between *cis* selectivity and chain length selectivity for the catalysts investigated here. W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT), the most Z-selective catalyst, also has the highest chain length selectivity. The least Z-selective catalyst, W(O)(CHCMe<sub>2</sub>Ph)(OHMT)<sub>2</sub>, yields a wide distribution of olefin chain lengths and has a poor chain length selectivity; however, this catalyst provides the highest amount of total product (1500 mmol versus 580 mmol for W(NAr)-(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT)).

Limitations in ISOMET conversions prompted us to screen variants of the Ru catalyst that contain other weakly coordinating counteranions. Using our optimized conditions, the counteranion seems to have a negligible effect on conversion or selectivity (Table 5). While the BARF<sub>4</sub> variant was used for much of this study, the (commercially available) PF<sub>6</sub> catalyst also appears to work well, as long as enough dichloromethane is present in the reaction mixture to keep the catalyst in solution.



**Table 4. Effect of W Metathesis Catalyst on Conversion and Selectivity<sup>a</sup>**

W cat <sup>c</sup>	<i>cis</i> -5-decene (mmol)	C10 (mmol)	% <i>cis</i> <sup>b</sup>	% chain length selectivity <sup>c</sup>	W TON <sup>d</sup>	Ru TON <sup>d</sup>
W(NAr)(C <sub>3</sub> H <sub>6</sub> ) (pyr) (OHIPT)	0.342	0.368	93%	64%	67	263
W(NAr') (C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub> (pyr) (OHIPT)	0.209	0.229	91%	57%	41	161
W(NAr)(CH- <i>t</i> -Bu) (Me <sub>2</sub> Pyr) (OHMT)	0.231	0.312	74%	34%	45	177
W(O) (CHCMe <sub>2</sub> Ph) (OHMT) <sub>2</sub>	0.043	0.281	15%	19%	8	33

<sup>a</sup>[CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup> (0.05 mol %), W cat (0.16 mol %), 350 mg *trans*-3-hexene, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 6h <sup>b</sup>Measured as the ratio of *cis*-5-decene versus the total C10 product formed. <sup>c</sup>Measured as the ratio of C10 product versus the total C7, C8, C9, and C10 product formed. <sup>d</sup>Calculated with respect to *cis*-5-decene. <sup>e</sup>Ar' = 2,6-dimethylphenyl; OHMT = O-2,6-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

**Table 5. Effect of Ru Isomerization Catalyst on Conversion and Selectivity<sup>a</sup>**

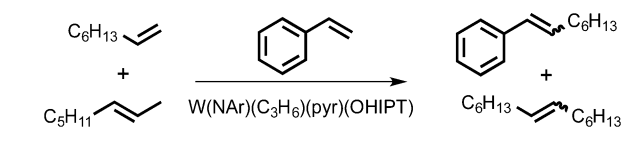
Ru cat	<i>cis</i> -5-decene (mmol)	C10 (mmol)	% <i>cis</i> <sup>b</sup>	% chain length selectivity <sup>c</sup>	W TON <sup>d</sup>	Ru TON <sup>d</sup>
[CpRu(P-N)(MeCN)] BAR <sub>4</sub> <sup>F</sup>	0.342	0.368	93%	64%	67	263
[CpRu(P-N)(MeCN)] PF <sub>6</sub>	0.277	0.291	95%	75%	54	212
[CpRu(P-N)(MeCN)] B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	0.398	0.438	91%	67%	78	306

<sup>a</sup>Ru (0.05 mol %), W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (0.16 mol %), 350 mg *trans*-3-hexene, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 6h. <sup>b</sup>Measured as the ratio of *cis*-5-decene versus the total C10 product formed. <sup>c</sup>Measured as the ratio of C10 product versus the total C7, C8, C9, and C10 product formed. <sup>d</sup>Calculated with respect to *cis*-5-decene.

Preliminary experiments suggested that Mo(NAr)-(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> was a poor candidate for ISOMET reactions (*vide supra*). In contrast to other metathesis catalysts, Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> could be employed in a closed vessel for ISOMET of *trans*-3-hexene; a wide distribution of olefins was observed when this Mo catalyst was paired with [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup> (see Figure S5 in the Supporting Information). The distribution of olefins qualitatively matches that observed in the reaction of the terminal olefin with a Mo olefin complex at high temperatures

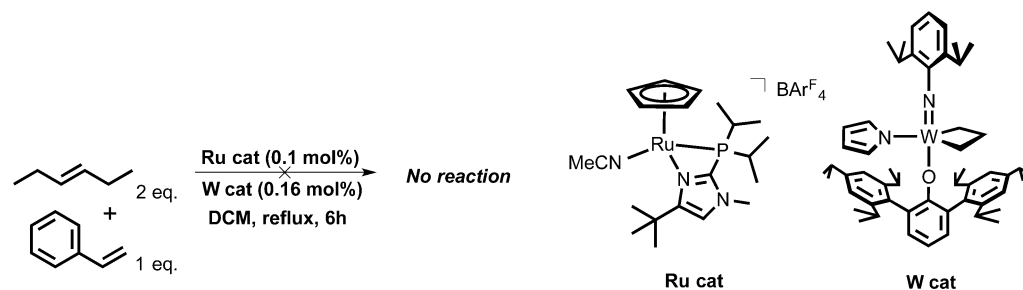
(where olefins are both isomerized and metathesized)<sup>21</sup> and approaches the product distribution observed in alkane metathesis. When Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> is used under conditions typically employed in an ISOMET reaction (refluxing dichloromethane under a continuous argon flow), an insoluble precipitate forms that we propose to be high molecular weight internal olefins; the precipitate was not characterized further. Light olefin products of olefin metathesis (<C<sub>6</sub>) are volatile enough to escape the apparatus, leaving heavier fragments in the vessel; several rounds of isomerization/metathesis would eventually produce longer, insoluble products.

**Cross-Metathesis Reactions.** A cross-metathesis ISOMET reaction was attempted in which styrene and *trans*-3-hexene were both added to the reaction mixture. Curiously, styrene completely inhibits any ISOMET reaction (Scheme 6). Styrene did not inhibit the isomerization of 1-hexene by [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup>, so the inhibition of ISOMET in the presence of styrene is apparently a metathesis related problem. In a separate competition experiment (Scheme 7), styrene (10

**Scheme 7. Competition Experiment between an Internal and a Terminal Olefin in Cross-Metathesis**

equiv), 1-octene (1 equiv), and *trans*-2-octene (1 equiv) were added to a C<sub>6</sub>D<sub>6</sub> solution of W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) at room temperature (Scheme 3). Within 24 h, isomers of 7-tetradecene and oct-1-en-1-yl-benzene could be observed by GC-MS; no 6-dodecene or hept-1-en-1-yl-benzene was formed. W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) reacts more readily with terminal olefins than internal olefins at room temperature, and under these conditions both cross-metathesis and homocoupling appear to be selective for terminal olefins. The reason why styrene inhibits ISOMET is still unclear.

Additional reactions were performed to see if other olefins inhibit ISOMET. In a mixture that contains *trans*-3-hexene and *cis*-2-heptene (4.16 mmol:0.845 mmol), 0.05 mol % [CpRu(P-N)(MeCN)]BAR<sub>4</sub><sup>F</sup>, and 0.16 mol % W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT), 0.431 mmol *cis*-5-decene was formed. On the basis of the amount of *cis*-2-heptene recovered from the reaction, 0.209 mmol *cis*-5-decene was formed through ISOMET. The remainder of the *cis*-5-decene was produced through homometathesis of *cis*-2-heptene, which suggests that this "terminal-olefin-selective" metathesis catalyst is also reactive toward *cis* internal olefins; its slow reaction with *trans* internal olefins is

**Scheme 6. Attempted Cross-Metathesis of Styrene and *trans*-3-Hexene**

what makes it valuable for ISOMET of *trans*-3-hexene. Remarkably, only trace amounts of C8 and C9 were formed, perhaps because the added *cis* olefin substrate increases the concentration of reactive (*cis* and terminal) olefins to compete with *trans* isomers.

A cross-metathesis ISOMET between *cis*-4-decene and *trans*-3-hexene was also attempted. A mixture of 0.371 mmol C10 (94% *cis*-5-decene) and 0.617 mmol C9 (91% *cis*-4-nonene) were formed, thus demonstrating that a cross-metathesis of *cis*-4-decene and 1-hexene is competitive with 1-hexene homocoupling during the ISOMET reaction.

**Factors That Affect Overall Conversion.** The ISOMET reaction does not proceed beyond 6 h; extending the reaction time to 24 h yielded essentially the same results as were observed after 6 h. The solution darkens after 6 h, suggesting that one of the catalysts decomposes or both catalysts decompose.

In a control experiment,  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$  was found to isomerize 1-hexene readily under ISOMET conditions without any sign of decomposition over a period of 6 h; the reaction color did not change, and upon adding additional 1-hexene, the catalyst continued to isomerize olefins to equilibrium mixtures. Thus,  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$  did not decompose in the absence of the metathesis catalyst. Every ISOMET reaction that was performed at 40 °C yielded hexene isomer ratios that are approximately what would be expected at equilibrium, which suggests that  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$  remains active throughout the ISOMET reaction. Although excessive  $\text{CH}_2\text{Cl}_2$  evaporation could lead to precipitation of  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$ , runs using larger amounts of  $\text{CH}_2\text{Cl}_2$  did not lead to higher levels of product. Also, addition of more  $\text{CH}_2\text{Cl}_2$  to the apparatus after 24 h did not result in additional conversion.

Decomposition of the metathesis catalyst could also cause ISOMET to stop.  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  is active for several days during alkane metathesis at 150 °C, and we therefore expected that this catalyst would not readily decompose during the ISOMET reaction (refluxing  $\text{CH}_2\text{Cl}_2$  at 40 °C). However, the concentration of olefin under AM conditions is very low at the steady state compared to ISOMET conditions, so a high olefin concentration may be responsible for a shorter catalyst life in some circumstances. Homometathesis of 1-hexene was previously reported with  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  at 4 mol % loading, achieving 35% conversion in 3 days at room temperature and 58% conversion in 24 h at 60 °C.<sup>22</sup> These reactions were performed in sealed J. Young NMR tubes. A homocoupling reaction of 1-hexene employing  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  under the same conditions as ISOMET (refluxing  $\text{CH}_2\text{Cl}_2$ , 24 h, argon flow) gave approximately 40% conversion. This TON (174) is more than the turnover number obtained during ISOMET with  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  (TON 60–80). The difference in TON between a homocoupling and an ISOMET reaction may be ascribable to the difference in concentration of terminal olefin in these two reactions.

While  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  decomposition seems to be a likely limitation in an ISOMET reaction, the addition of more  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  and  $\text{CH}_2\text{Cl}_2$  after 24 h did not lead to an increase in conversion (0.230 mmol total *cis*-5-decene).  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$  may also decompose under ISOMET conditions, but at this stage decomposition of  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  appears to be faster under the conditions employed. The equilibrium mixture of remaining

hexenes obtained at the end of ISOMET reactions supports this hypothesis.

## CONCLUSIONS

ISOMET has been demonstrated for the preparation of Z-internal olefins from a mixture of *trans* olefin isomers. We have demonstrated that certain metathesis catalysts can discriminate terminal from internal olefins, and that Z-selectivity and chain length selectivity of a given catalyst in ISOMET reactions are related qualitatively. Chain length selectivity in ISOMET appears to be higher than in AM reactions. The factors that limit conversion in ISOMET reactions are not understood, but decomposition of the metathesis catalyst in the presence of the Ru catalyst is the lead suspect. A more robust metathesis catalyst and catalysts that can function in a tandem reaction at room temperature would be highly desirable and should boost selectivity and catalyst longevity.

## EXPERIMENTAL SECTION

All manipulations were conducted under a nitrogen or argon atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques, unless otherwise specified. All glassware was oven-dried prior to use. Ether, pentane, toluene, and benzene were degassed with nitrogen and passed through activated alumina columns under nitrogen. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen or argon-filled glovebox. NMR spectra were recorded on 300, 500, or 600 MHz spectrometers at room temperature. Chemical shifts for  $^1\text{H}$  spectra were referenced to the residual resonances of the deuterated solvent and are reported as parts per million relative to tetramethylsilane.  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$ ,<sup>11e</sup>  $\text{W}(\text{NAr}')(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$ ,<sup>22</sup>  $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{Me}_2\text{Pyr})(\text{OHMT})$ ,<sup>2</sup> and  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OHMT})_2$ <sup>23</sup> were prepared using literature procedures.

**Representative ISOMET Procedure.** Under a nitrogen atmosphere,  $[\text{CpRu}(\text{P}-\text{N})(\text{MeCN})]\text{BAR}^{\text{F}_4}$  (3.4 mg, 2.6  $\mu\text{mol}$ ),  $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{pyr})(\text{OHIPT})$  (5.0 mg, 5.2  $\mu\text{mol}$ ), *trans*-3-hexene (350 mg),  $\text{CH}_2\text{Cl}_2$  (~100  $\mu\text{L}$ ), mesitylene, and a stir bar were added to a 25 mL glass vessel equipped with reflux condenser and two Teflon valves. The reactor was filled with argon and a slow flow rate maintained as the reaction was heated in an oil bath until the dichloromethane vigorously refluxed. After 6 h, the reaction mixture was passed through basic alumina, and the resulting solution was subjected to GC-FID analysis (Agilent CP-Sil PONA CB, 50 m, 0.21 mm; He carrier gas; 35 °C isothermal, 240 min; 100:1 split; crude samples diluted with  $\text{C}_5\text{H}_{12}$  25:1). The peaks were integrated with respect to the mesitylene internal standard. GC response factors were calculated with C6–C10 olefin standards.

**Synthesis of 1-Nonene.** A suspension of methyltriphenyl phosphonium bromide in THF was prepared in a Schlenk flask. The flask was cooled to 0 °C, and *n*-BuLi (2.5 M in hexanes) was added dropwise. The resulting red-orange suspension was cooled to –78 °C, and after 15 min, octanal (used as received) was added dropwise. The reaction was allowed to warm to ambient temperature. After 16 h, water and pentane were added, and the organic layer was washed with water and dried over  $\text{MgSO}_4$ . Reduction of the solvent volume, followed by passage through a silica plug (pentane eluent) and evaporation of volatile components, afforded the product. The spectrum of the product matched literature values.<sup>24</sup>

### Olefin Cross-Metathesis Competition Experiment.

Styrene (16.5 mg, 0.159 mmol), 1-octene (3.6 mg, 0.032 mmol), and *trans*-2-octene (3.6 mg, 0.032 mmol) were added to a C<sub>6</sub>D<sub>6</sub> solution of W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (2.5 mg, 2.6 μmol) at room temperature. The reaction was run in a small uncapped vial within a larger, capped 20 mL scintillation vial, which provided additional headspace for any ethylene that was generated. After 24 h, isomers of 7-tetradecane and oct-1-en-1-yl-benzene can be observed by GC-MS.

**Olefin Homometathesis Competition Experiment.** A mixture of 1-octene and *trans*-2-octene was added to a C<sub>6</sub>D<sub>6</sub> solution containing W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (2.5 mg, 2.6 μmol) or Mo(NAr)(CHCMe<sub>2</sub>Ph)[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (2.5 mg, 3.3 μmol) at room temperature. The reaction was run in a small uncapped vial within a larger, capped 20 mL scintillation vial, which provided additional headspace for any generated ethylene. The reactions were stopped after 2 h and analyzed by <sup>1</sup>H NMR.

**Ru-Catalyzed Olefin Isomerization.** Under a nitrogen atmosphere, [CpRu(P-N)(MeCN)]BAR<sup>F</sup><sub>4</sub> (3.4 mg, 2.6 μmol), 1-hexene (350 mg), CH<sub>2</sub>Cl<sub>2</sub> (~100 μL), mesitylene, and a stir bar were added to a 25 mL glass vessel equipped with reflux condenser and two Teflon valves. The reactor was placed under an Ar atmosphere and heated in an oil bath until the dichloromethane refluxed vigorously. The reaction was stopped after 6 h, and an aliquot was taken and analyzed by <sup>1</sup>H NMR. An additional 350 mg of 1-hexene was added and the reactor was heated for another 19 h. An aliquot of the final reaction mixture confirmed that 1-hexene had been isomerized to an equilibrium mixture of 1-hexene, *trans*-2-hexene, and *trans*-3-hexene. These values matched theoretical values obtained from a calculation that employed standard enthalpies of formation.

**Styrene/Hexene ISOMET Procedure.** Under a nitrogen atmosphere, [CpRu(P-N)(MeCN)]BAR<sup>F</sup><sub>4</sub> (1.7 mg, 1.3 μmol), W(NAr)(C<sub>3</sub>H<sub>6</sub>)(pyr)(OHIPT) (5.0 mg, 5.2 μmol), *trans*-3-hexene (250 mg), styrene (100 mg), CH<sub>2</sub>Cl<sub>2</sub> (~100 μL), mesitylene, and a stir bar were added to a 25 mL glass vessel equipped with reflux condenser and two Teflon valves. The reactor was placed under an Ar atmosphere and heated in an oil bath such that the solution refluxed vigorously. After 6 h, the reaction mixture was passed through basic alumina, and the resulting solution was subjected to GC analysis. No cross products or new olefin lengths were observed.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

GC traces for the ISOMET reaction and the synthesis and characterization of Ru complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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